

VAPOR PHASE GROWTH TECHNIQUE AND SYSTEM
FOR
SEVERAL III-V COMPOUND SEMICONDUCTORS

by

J. J. Tietjen, R. Clough, and D. Richman

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Dr. S. Fischler
Technical Monitor
NAS 12-538
Electronics Research Center
575 Technology Square
Cambridge, Massachusetts 02139

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Summary

The objective of this contract is a single vapor phase growth system to prepare GaP, GaAs, InSb, InP, InAs, InSb, and selected alloys of these compounds. In addition, the system should provide for n- and p-type doping and the preparation of multilayer structures. An RCA method used to prepare GaAs, GaP, and their alloys is being extended for the growth of compounds and alloys containing In and Sb.

The work is progressing satisfactorily. Three separate vapor growth systems have already been put into operation to facilitate the research. The growth parameters for InAs and InP were investigated, and adequate growth rates for single-crystalline layers were achieved. In addition, an $\text{In}_{.1}\text{Ga}_{.9}\text{As}$ alloy single-crystal layer has been prepared in a system in which, for the first time, the In and Ga sources were maintained at different temperatures. InAs has also been prepared as both n- and p-type layers; initial characterization shows it to be of high quality. Because stibine has not yet been available, an alternate method such as chloride transport of Sb metal may be selected.

I. INTRODUCTION

The objective of this contract is to develop a compatible vapor phase growth method for the preparation of several III-V compound semiconductors involving the elements Ga, In, P, As, and Sb. In addition, this method should facilitate n- and p-type doping and the preparation of multilayer structures. In previous research, RCA had demonstrated the ability to prepare GaAs, GaP, and their alloys, with outstanding properties relative to this goal, using a unique vapor phase growth technique.¹ This method is now being extended to permit the growth of compounds containing In and Sb.

In order to efficiently achieve this objective, three separate growth systems are presently being used: one to study In transport, a second to study incorporation of Sb in the growth process, and a third for the study of simultaneous transport of Ga and In. Each of these systems has been slightly changed from the standard design to facilitate these specifications; but the individual modifications are minor and can easily be incorporated in a single system. Since manufacturer's delays in supplying stibine have interfered with the studies relating to Sb, the second system is currently being used in conjunction with the first to accelerate the In transport studies.

The construction of all of these growth systems was virtually completed prior to the start of this contract, and only minor alterations and final testing were required to make them available for this program. Therefore, our previous work and experience have enabled us to be well ahead of anticipated contract schedules.

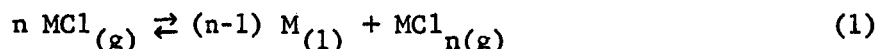
To date, single-crystalline InAs, InP, and $\text{In}_{1-x}\text{Ga}_x\text{As}$ alloys have been prepared with adequate growth rates, and n- and p-type doping of InAs has been achieved. It is particularly noteworthy that undoped InAs has room-temperature electrical properties which compare favorably with the best material previously reported.

II. TECHNICAL DISCUSSION

A. General Chemistry

An understanding of the chemistry involved in vapor phase transport systems is essential for the proper design of experiments and equipment. This is particularly important for the growth of alloys of gallium and indium compounds, since the thermodynamics pertinent to the chemical transport of these two elements is markedly different. For example, in a recent publication,² the growth of $\text{Ga}_x\text{In}_{1-x}\text{As}$ alloys was described using apparatus in which both the gallium and indium sources were maintained at the same temperature in the same furnace. We believe that this approach is not desirable, and we hope to attain much better control over alloy composition by using a differently designed vapor growth system. In addition, accordingly, we are separately investigating the conditions for attaining proper InAs and InP deposition rates and crystalline quality.

The chemistry here involves the transport of gallium and indium via disproportionation reactions of their subchlorides. A typical reaction is illustrated in Eq. (1) where M may be Ga or In and n may be 2 or 3 depending upon the temperature and reactant concentrations.



High temperatures favor the left side of this reaction, low temperatures the right. In using this reaction to prepare a III-V compound, the monochloride is formed by reaction of the metal with HCl and then carried to a deposition zone where reaction (1) occurs in the presence of a group V element (such as As or P) giving the III-V compound rather than the metal.

While the principle applies equally well to Ga or In, the stability of the monochloride relative to higher chlorides differs greatly between them. The low stability of GaCl allows Ga to be efficiently transported with a temperature difference between the source and deposition zones of only 50°C. However, the high stability of InCl requires much larger temperature differences (of the order of 200°C or more) to achieve comparable efficiencies. A second factor related to the difference in stabilities is that, whereas in the Ga case volatile GaCl_3 is the major constituent of the gas phase, in the In case InCl is the major component. This compound is much less volatile than GaCl_3 and care must be taken to avoid condensation at low deposition temperatures.

Both of these factors indicate that higher source temperatures and larger gradients are required for the efficient transport of In compounds. In addition, for the simultaneous transport of In and Ga, it is important to allow for different source temperatures for these two elements, and to minimize the possibility of re-equilibration of the respective chlorides.

In selecting appropriate deposition temperatures for In compounds, consideration must be given not only to the vapor pressure of InCl, but to the dissociation pressure of the deposited material. For example, InP has a high

dissociation pressure above about 750°C and, therefore, a low deposition temperature is desirable. It is evident that the final conditions chosen must represent the best compromise of the various factors involved.

B. Growth of InAs

The first of the above-mentioned systems has been converted from one used to prepare $\text{GaAs}_{1-x}\text{P}_x$ alloys to one for the growth of indium-base III-V compounds. This involved substituting In for Ga in the source region of the apparatus. The system, otherwise identical to that described previously,¹ is shown schematically in Figure 1.

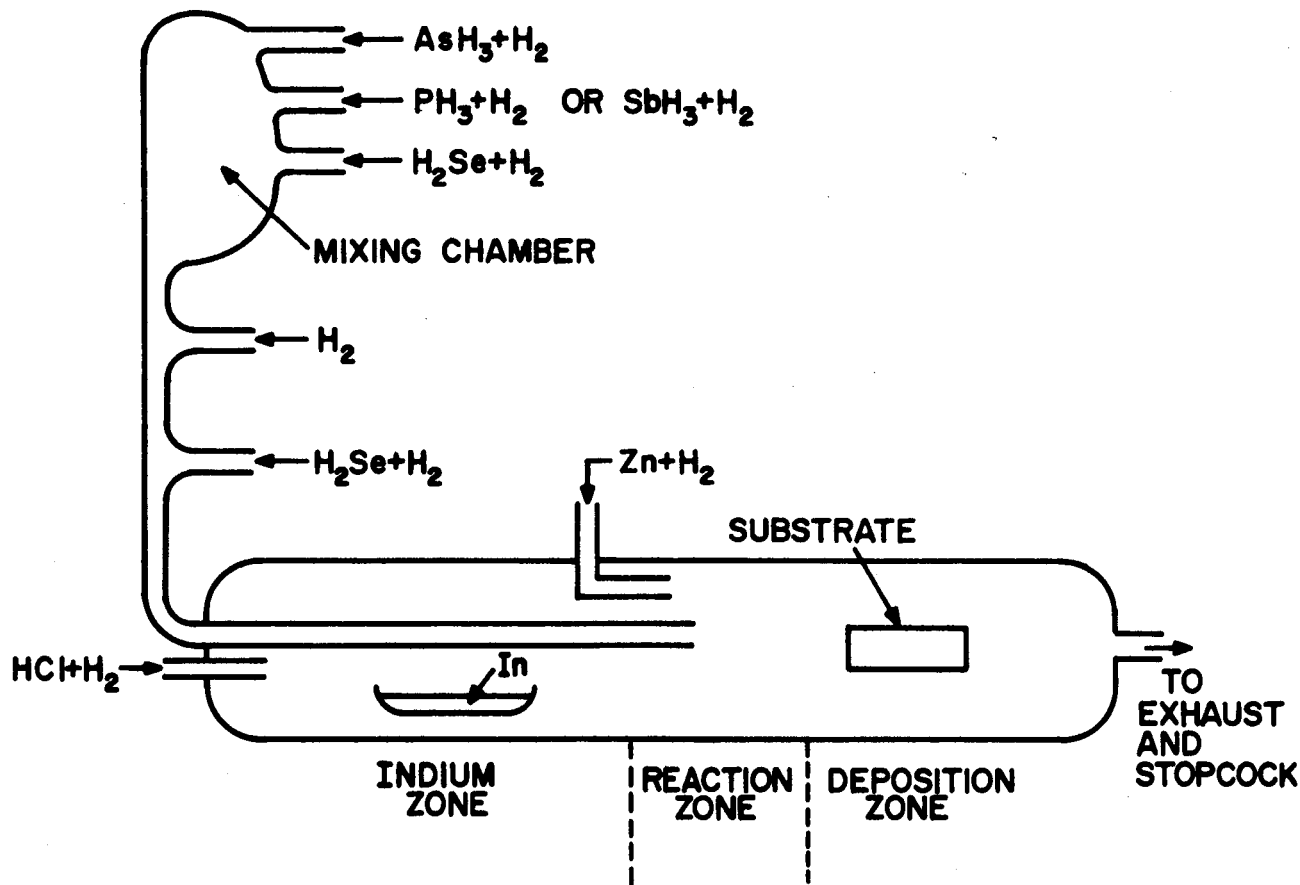


Figure 1. Schematic representation of vapor-deposition apparatus.

A series of experiments were performed to optimize the growth rate of InAs. The growth parameters studied were flow rates of the gaseous reactants, temperatures throughout the growth system, and substrate material. The results of these studies are presented in Table I.

TABLE I
GROWTH OF InAs

Growth of Epitaxial InAs on GaAs									
Run Number	Substrate Orientation	Furnace Temp., °C			Flow Rates, cm ³ /min			Growth Rate, μ m/hr	Comments
		Deposition Zone	Center Zone	Indium Zone	H ₂ Carrier for HCl	H ₂ Carrier for AsH ₃	10% AsH ₃ in H ₂		
4-28-67-M	(100)	625	950	850	1100	1300	200	3.1	
5-2-67-M1	(100)	625	950	850	300	600	100	nil	
5-2-67-M2	(100)	625	950	850	700	1100	200	4.1	
5-5-67-M2	(100)	700	950	850	300	600	100	14.0	
5-5-67-M1	(100)	725	950	850	300	600	100	15.3	
4-25-67-M	(100)	725	950	850	1100	1300	200	19.0	
4-26-67-M	(100)	725	950	850	1100	1300	200	25.4	
5-9-67-M1	(100)	725	950	850	300	600	200	28.0	
5-9-67-M2	(100)	725	950	850	300	600	200	28.0	
5-4-67-M	(100)	750	950	850	1100	1300	100	12.7	
5-8-67-MA	(100)	750	950	850	300	600	100	10.2	
5-8-67-MB	(100)	750	950	850	300	600	100	7.1	Substrate 1 in. to right of center of furnace.
5-8-67-MC	(100)	750	950	850	300	600	100	5.1	Substrate 2 in. to right of center of furnace.
Growth of Homoepitaxial InAs									
5-10-67-M	(100)	725	950	850	300	600	200	25.0	
5-15-67-M	(100)	725	950	850	300	600	200	30.0	
5-23-67-M	(100)	725	950	850	300	600	200	37.0	Doped with Zn
5-24-67-M	(100)	725	950	850	300	600	200	22.0	Doped with Zn
5-31-67-M	(110)	725	950	850	300	600	200	11.0	
6-14-67-M	(100)	725	950	850	300	600	200	20.0	Doped with Se

The thermodynamic arguments presented in Section II.A. suggest the use of a steeper temperature gradient than has been used in the GaAs system. Temperatures of 725°C for the deposition zone, 950°C for the center zone, and 850°C for the indium zone were used. These temperatures, together with the flow rates for the gaseous reactants used in the GaAs system, resulted in reasonably rapid growth rates (20-25 microns/hr) on (100)-oriented GaAs substrates (runs 4-25-67M and 4-26-67M). X-ray analysis confirmed that the deposited layers were single-crystal epitaxial InAs. It is evident that changing the flow conditions within broad limits does not significantly affect the growth rate; but, as described in Section II.A., thermal conditions play a very important role. At lower deposition zone temperatures the growth rate was greatly reduced, perhaps due to enhanced liquification of indium chlorides in the

deposition zone. The growth rate was also reduced at higher deposition zone temperatures, owing to the greatly increased stability of InCl relative to that of InCl_3 . Suitable flow rates were found to be $300 \text{ cm}^3/\text{min}$ for the HCl carrier gas and $600 \text{ cm}^3/\text{min}$ for the AsH_3 carrier. It was found that a minimum flow rate of a 10% AsH_3 -in- H_2 mixture of $200 \text{ cm}^3/\text{min}$ was necessary for reasonable growth rates, and that the growth rate did not increase above this flow rate. Gaseous HCl was introduced at the constant rate of $4.0 \text{ cm}^3/\text{min}$.

Following epitaxial growth studies of InAs on GaAs substrates, homoepitaxial InAs was deposited on (100) and (110)-oriented InAs substrates. In order to prepare the surfaces for growth, a series of etchants were investigated and it was found that room-temperature bromine-methanol etches are suitable for polishing InAs on the (100) and (110) surfaces. Using a rotating beaker polishing apparatus, the (100)-oriented InAs substrates were polished for 15 min in a 1% solution of bromine in methanol, and the (110)-oriented InAs substrates were polished in a 2% solution of bromine in methanol for 15 min. To date, a suitable chemical polish for (111) InAs surfaces has not been obtained. Better surfaces were exhibited by growths of homoepitaxial InAs than by epitaxial growths on GaAs , which has a 5.1% degree of lattice constant misfit with InAs . Some pits, however, similar to those grown in homoepitaxial GaAs , were formed in the homoepitaxial (110)-oriented InAs . The growth rate on (100)-oriented InAs was nearly the same as on (100)-oriented GaAs , but the growth rate on (110)-oriented InAs , however, was about half that rate. The first grown layers are n-type and have net carrier concentrations of less than $5 \times 10^{16}/\text{cm}^3$ and mobilities as high as $29,000 \text{ cm}^2/\text{V-sec}$ at 300°K , which are comparable to good melt-grown material and the best yet obtained at 300°K for vapor-grown InAs . Difficulties in maintaining ohmic contacts at low temperatures, and the inherent brittleness of the InAs Hall samples, have so far prevented measurements at 77°K .

Both n- and p-type doping of InAs has been achieved using Se and Zn as the respective dopants. The electrical properties of these layers have not yet been evaluated.

C. Growth of InP

As previously pointed out, a second system has been newly constructed to incorporate stibine (SbH_3) for the growth of Sb compounds. It is essentially identical to that shown in Figure 1, except that provisions have been added for the future incorporation of antimony. This system has been proven acceptable for experimental use by growing homoepitaxial GaAs with a net carrier concentration of $6.5 \times 10^{15}/\text{cm}^3$ and a mobility of $21,100 \text{ cm}^2/\text{V-sec}$ at 77°K . Owing to a manufacturer's delay in the delivery of the stibine, this system is presently being used to grow InP ; meanwhile, consideration is being given to transporting Sb via its chlorides.

The results of a series of experiments to establish temperatures and flow rates for good InP growth rates are given in Table II. The growth rates are given as an average growth over both surfaces of the substrates since there was some variation in thickness of the grown layers. The layers, deposited on

TABLE II
GROWTH OF EPITAXIAL InP ON GaAs

Run Number	Furnace Temp., °C			Flow Rates, cm ³ /min			Avg. Growth Rate, microns/hr
	Deposition Zone	Center Zone	Indium Zone	H ₂ carrier for HCl	H ₂ carrier for PH ₃	5% PH ₃ in H ₂	
5-22-67-6	650	950	850	500	400	400	7.6
5-19-67-C2	675	950	850	500	400	400	10.0
5-23-67-C	675	950	900	500	400	400	8.0
5-26-67-C	675	950	900	500	400	400	10.03
5-24-67-C	675	950	900	500	400	400	11.4
5-16-67-C	700	950	850	500	400	400	9.2
5-19-67-C1	700	950	850	500	0	800	9.2
5-17-67-C	700	950	850	500	400	800	3.0

(100)-oriented GaAs, were shown to be single-crystal epitaxial InP by x-ray analysis, and preparations are being made to make measurements of their electrical properties.

As expected from the thermodynamic arguments given above, a low deposition zone temperature (675°C) and high indium zone temperature (900°C) were necessary for reasonable growth rates. The center zone was held at 950°C. It was found that high H₂ carrier gas flow rates decreased the growth rate, since the resulting dilution further stabilizes InCl and also reduces the phosphorus pressure. The H₂ carrier gas for the HCl was fed at 500 cm³/min and the H₂ carrier gas for the PH₃ was fed at 400 cm³/min. In similarity to the InAs system, it was found that 400 cm³/min of a 5% PH₃-in-H₂ mixture was necessary for a reasonable growth rate, and that higher PH₃ flow rates did not increase the growth rate. The HCl flow rate was maintained constant at 4.0 cm³/min.

Since the maximum InP growth rates are only 1/2 that obtained for InAs, even steeper temperature gradients will be investigated in the future.

D. Growth of In_{1-x}Ga_xAs Alloys

A third system has been constructed which allows the independent control of the temperature and gas atmosphere passing over two separate source metals. A diagram of this system is shown in Figure 2. The significant modifications of a standard system which have been incorporated in this system are (a) an

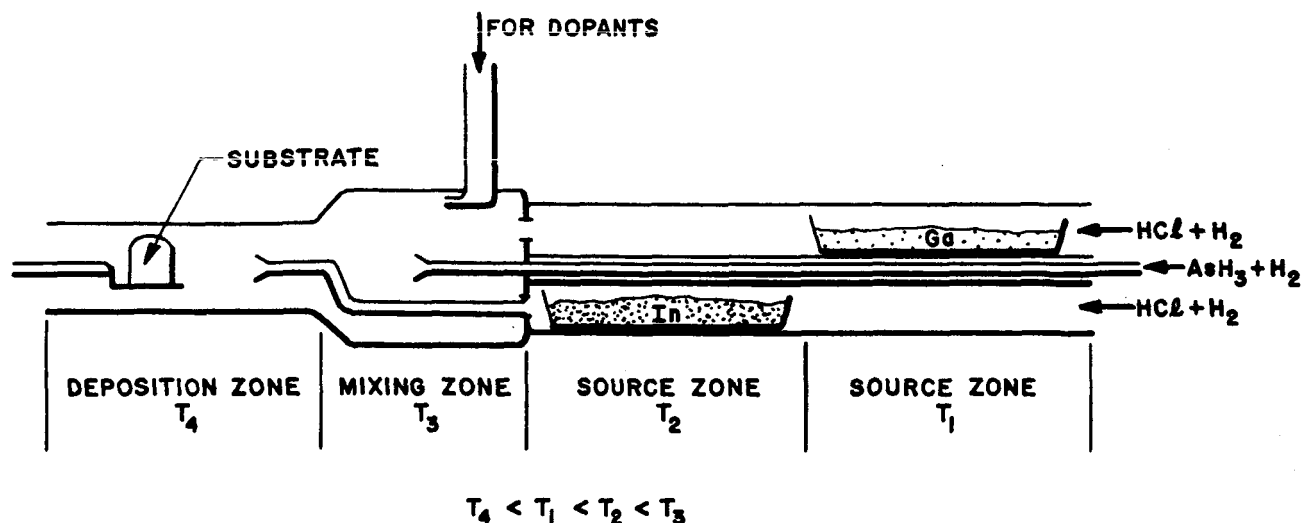


Figure 2. Apparatus for the growth of $\text{In}_{1-x}\text{Ga}_x\text{As}$ alloys.

elongation of the source zone so that two independently controlled 8-in. furnace sections may be used, and (b) the standard 26-mm ID reaction tube of the source region has been replaced by two 15-mm ID tubes placed one over the other. The effluents from these two source tubes are arranged so that one feeds directly into the mixing zone whereas the other bypasses the mixing zone and discharges into the main gas flow in the deposition zone approximately 1 inch upstream from the substrate. This geometry was chosen to minimize reactions between the source gases before deposition on the substrate.

The discussion in Section II.A. of the chemistry involved in transporting the group III metals shows that this system is ideally suited for the growth of III-V compound alloys containing mixed group III metals. In order to demonstrate this feasibility work has been started on the growth of $\text{In}_{1-x}\text{Ga}_x\text{As}$. Because this equipment became available late in the report period only one run has been made. However, this yielded very encouraging results.

The experimental conditions are summarized in Table III and the results are shown in Table IV. The composition was inferred from optical absorption measurements and the data of Hockings et al.³ on bandgap vs. composition. It should be noted that this alloy is considerably richer in In than alloys prepared by Conrad et al.² with equal chloride flows over Ga and In sources at the same temperature. Our results would be anticipated from our previous discussions of the pertinent chemistry.

Unfortunately, it was not possible to measure the low-temperature electrical properties of this specimen. Any conclusions or speculations about the electrical properties of alloys grown by the technique would be premature at this time.

TABLE III

EXPERIMENTAL CONDITIONS FOR THE GROWTH OF $\text{In}_{1-x}\text{Ga}_x\text{As}$
[GaAs SUBSTRATE (100)-SURFACE]

Zone	Temperature ($^{\circ}\text{C}$)	Gas	Flow (cm^3/min)
Ga	795	HCl	3
		H_2	380
In	905	HCl	3
		H_2	380
Mixing	920	10% AsH_3 in H_2	200
		H_2	760
Deposition	709	plus Effluent from Ga Zone All above	

TABLE IV

ROOM-TEMPERATURE PROPERTIES OF InAs-GaAs ALLOY
GROWN EPITAXIALLY ON GaAs

Composition	90% GaAs, 10% InAs
Carrier Concentration	1×10^{15} electrons/ cm^3
Resistivity	1.37 ohm-cm
Mobility	$4400 \text{ cm}^2/\text{V-sec}$

III. CONCLUSIONS AND RECOMMENDATIONS

The development of a compatible vapor phase growth method for preparing several III-V compounds is progressing at a satisfactory rate. InAs, InP, and a $\text{In}_{.1}\text{Ga}_{.9}\text{As}$ alloy have already been prepared. In addition InAs has been prepared as both n- and p-type layers, and initial characterization of InAs has indicated that this material is of high quality. Since the commercial supplier of stibine has encountered difficulties in preparing and storing stibine, we have not yet received any shipment. This may necessitate selecting an alternative method such as chloride transport of Sb metal.

During the next quarter, work will continue on preparing InAs, InP, and $\text{In}_{1-x}\text{Ga}_x\text{As}$ and will include doping these materials with both donor and acceptor impurities. In addition, Sb will be added to the growth system to permit preparation of GaSb and InSb. Also, $\text{InAs}_{1-x}\text{P}_x$ and $\text{Ga}_{1-x}\text{In}_x\text{P}$ alloys will be prepared. Finally, efforts will continue to make low-temperature Hall measurements on these materials to evaluate their purity.

IV. REFERENCES

1. J. J. Tietjen and J. A. Amick, J. Electrochem. Soc. 113, 724 (1966).
2. R. W. Conrad, P. L. Hoyt, and D. D. Martin, J. Electrochem. Soc. 114, 164 (1967).
3. E. F. Hockings et al., J. Appl. Phys. 37, 2879 (1966).

V. NEW TECHNOLOGY APPENDIX

A. Title: Chemical Polishing of (100) and (110) InAs Surfaces

Page Reference: 6

Comments: No chemical etchants have yet been reported for polishing InAs. The etchant described is especially useful for providing smooth, damage-free, clean surfaces of InAs for epitaxial growth.

B. Title: Improved Procedure for the Growth of $\text{In}_{1-x}\text{Ga}_x\text{As}$ Alloys

Page Reference: 7, 8

Comments: In previous vapor phase growth systems, the indium and gallium have either been mixed together, or have been maintained at the same temperature in the same furnace. Here, the indium and gallium sources are held at separate temperatures, and this allows superior control over the composition of the grown $\text{In}_{1-x}\text{Ga}_x\text{As}$ alloys.

Note: Although the etchant described under A. and the growth system described under B. are not new in themselves, their application to InAs and $\text{In}_{1-x}\text{Ga}_x\text{As}$ alloys is new.